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(54) Title: PROCESS FOR COATING A SURFACE

(57) Abstract: A method of forming a coating of polyionic materials in a layer-by-layer-like manner onto a polymeric material is provided. A polymeric material, such as a contact lens, can be dipped once into a solution of polyionic materials such that layers of polyionic material can be formed thereon. A single dip solution of the present invention typically contains a polyanionic material and a polycationic material in a non-stoichiometric amount and maintained within a certain pH range.

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Process for coating a surface

The present invention generally relates to a method of treating polymeric materials, such as biomedical devices and contact lenses. In particular, the present invention is directed to a method of altering the hydrophobic or hydrophilic nature of the polymeric surface of a biomedical device by applying a single-dip polyionic solution to form a layer-by-layer-like coating thereon.

Many devices used in biomedical applications require that the bulk of the device have one property, while the surface of the device has another property. For example, contact lenses may have high oxygen permeability through the lens to maintain good corneal health. However, materials that exhibit exceptionally high oxygen permeability (e.g. polysiloxanes) are typically hydrophobic and will adhere to the eye. Thus, a contact lens generally has a core or bulk material that is highly oxygen permeable and hydrophobic, and a surface that has been treated or coated to increase hydrophilic properties, thereby allowing the lens to freely move on the eye without adhering excessive amounts of tear lipid and protein.

In order to modify the hydrophilic nature of a relatively hydrophobic contact lens material, a contact lens can be treated with a plasma treatment. For example, a plasma treatment technique is disclosed in PCT Publication No. WO 96/31793. Some plasma treatment processes, however, require a significant monetary investment in certain equipment. Moreover, plasma treatment requires that the lens be dry before exposure to the plasma. Thus, lenses that are wet from prior hydration or extraction processes must be dried, thereby imposing added costs of obtaining drying equipment, as well as added time in the overall lens production process.

As a result, a number of methods of consistently and permanently altering the surface properties of polymeric biomaterials, such as contact lenses, have been developed. PCT Publication WO 99/35520 describes the layer-by-layer ("LbL") polymer absorption process. The process involves consecutively dipping a substrate into oppositely charged polyionic materials until a coating of a desired thickness is formed. Nevertheless, although this technique provides an effective polyelectrolyte deposition technique for biomaterials, such as contact lenses, a need for further improvement still remains. For example, with this

layer-by-layer dipping process, a coating could require multiple dipping steps that take a substantial amount of time to apply. As a result, manufacturing costs can often be increased due to the amount of time and dipping required to sufficiently coat the substrate.

As such, a need currently exists for an improved method of coating a material, such as a contact lens, with polyelectrolyte (polyionic) layers. In particular, a need exists for an improved polyionic deposition technique that requires less time and dipping than the previously-described layer-by-layer deposition technique.

Accordingly, an object of the present invention is to provide an improved method of treating polymers, such as ophthalmic lenses, to alter surface properties.

It is another object of the present invention to provide an improved method of treating polymers with polyionic materials to alter the hydrophilic or hydrophobic nature of their surfaces.

Still another object of the present invention is to provide an improved method of coating a polymer substrate with a polyionic material to alter the surface properties of the substrate. Yet another object of the present invention is to provide an improved method of coating a polymer substrate with a polyanionic and a polycationic material.

Another object of the present invention is to provide a method of coating a polymer substrate with layers of a polyanion and polycation in a relatively short period of time.

It is another object of the present invention to provide a method for applying layers of a polyanion and polycation to a substrate in a single dip.

These and other objects of the present invention are achieved by providing a method for applying a polyionic solution to a substrate material, such as a contact lens. The method of the present invention can, in most embodiments, apply successive layers of polyionic material onto the substrate with only a single dip of the substrate into the polyionic solution.

The invention thus in one aspect relates to a method of coating a polymeric substrate comprising the steps of:

forming a solution, said solution containing a negatively charged material and a positively charged material in an amount such that the molar charge ratio of said solution is from about 3:1 to about 100:1;

maintaining the pH of said solution within a range so that said negatively charged material and said positively charged material remain stable within said solution; and

applying said solution to said substrate to form a coating thereon, said coating on said substrate having at least two layers so that one of said layers comprises said negatively charged material and another of said layers comprises said positively charged material.

In accordance with the present invention, a polyionic solution is employed to coat the substrate. In general, the polyionic solution contains at least one polycationic material and at least one polyanionic material, although more than one of each polyionic material can be employed. In one embodiment, for example, the polyionic solution is a bicomponent solution containing a polycation and a polyanion.

Typically, a polycationic material of the present invention can include any material known in the art to have a plurality of positively charged groups along a polymer chain. For example, in one embodiment, the polycationic material includes poly(allyl amine hydrochloride).

Likewise, a polyanionic material of the present invention can typically include any material known in the art to have a plurality of negatively charged groups along a polymer chain. For example, in one embodiment, the polyanionic material includes polyacrylic acid.

According to the present invention, a polycationic material is combined with a polyanionic material to form the polyionic solution. In general, the polyionic components are added in non-stoichiometric amounts such that one of the components is present within the solution in a greater amount than another component. In particular, the molar charge ratio, as defined herein, can be from about 3:1 to about 100:1. In certain embodiments, the molar charge ratio is 10:1 (polyanion:polycation).

By increasing the molar charge ratio, a polyionic solution of the present invention can be "self-cascaded" onto a substrate. In other words, when the substrate is dipped into the solution, alternating layers of polyionic components can be coated onto the substrate. For example, in one embodiment, polyanionic-polycationic-polyanionic alternating repeating layers are assembled when the substrate is dipped into the solution.

Besides containing polyionic components, a polyionic solution of the present invention can also contain various other materials. For example, the polyionic solution can contain antimicrobials, antibacterials, radiation-absorbing materials, cell growth inhibitors, etc.

In accordance with the present invention, it is typically desired to maintain the pH of the solution within a certain range. Maintenance of pH can help prevent precipitation of one of the polyionic components from solution. Accordingly, in one embodiment, the pH is maintained within about ± 0.5 of an appropriate pH. Preferably, the pH is maintained within about ± 0.1 of an appropriate pH. In general, the appropriate pH for a given solution is at least partially dependent on the polyionic materials selected and can be determined by any suitable method known in the art.

As noted above, after forming the polyionic solution according to the present invention, a substrate material is generally dipped into the solution such that it becomes sufficiently coated. In general, a substrate material of the present invention can be made from any polymeric material. In particular, a substrate material of the present invention can be made from oxygen-permeable polymeric materials. For example, some examples of suitable substrate materials, include, but are not limited to, the polymeric materials disclosed in U.S. Patent No. 5,760,100.

In some embodiments, the substrate can also be preconditioned to enhance the ability of the polyionic solution to coat the substrate. In one embodiment, for example, a layer-by-layer application process can be used to form an underlayer or primer coating on the substrate. This underlayer can sufficiently roughen the surface such that the ultimate single-dip coating solution of the present invention can better adhere to the substrate surface.

Moreover, in another embodiment, a solvent solution can be initially applied to the substrate for preconditioning. The application of a solvent, such as an alcohol solution, in the presence of a polyionic component or multiple polyionic components, can allow the substrate to swell. After swelling, the substrate can then be removed from the solvent solution and then dipped into a polyionic solution so that it shrinks. The shrinking of the substrate can entrap the polyionic component(s) within the substrate. As a result, in some

embodiments, the ultimate single-dip solution of the present invention more easily adheres to the substrate surface when applied thereto.

In contrast to the heretofore-mentioned layer-by-layer processes, a process of the present invention can apply alternating layers of a polyionic solution to a substrate with only a single dip, thus saving a substantial amount of time. For example, coatings of from about 40 angstroms to about 1000 angstroms can be applied in a single dip. Moreover, the time for applying such coating can be less than 6 minutes and even as little as 1 minute. Other objects, features and aspects of the present invention are discussed in greater detail below.

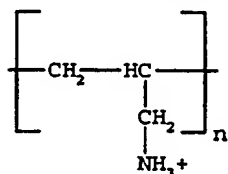
Reference now will be made in detail to the embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their equivalents. Other objects, features and aspects of the present invention are disclosed in or are obvious from the following detailed description. It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention.

In general, the present invention is directed to an improved method of coating substrate materials, such as contact lenses, with a solution of negatively and positively charged materials, such as polyionic materials. In particular, the present invention is directed to a process employing a coating solution that includes both a polycation and polyanion maintained at a certain pH level. It has been discovered that a process of the present invention can sufficiently coat a substrate material with a certain thickness of polyionic layers in a substantially less time period than prior coating processes. For example, in one embodiment, a single dip process of the present invention can be employed to provide a 100 angstrom thick coating in about 6 minutes.

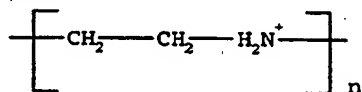
In accordance with the present invention, a coating process is provided that can be utilized to deposit polyionic materials onto a substrate. In one embodiment, for example, a process of the present invention allows the deposition of a bicomponent polyionic solution to a biomaterial substrate, such as a contact lens.

To form a coated substrate of the present invention, a coating solution is initially formed. As stated, a coating solution of the present invention can include polyionic materials, such as polyanionic or polycationic materials. For instance, a first material may be a polycationic material, which can include any material known in the art to have a plurality of positively charged groups along a polymer chain. Such materials can include, but are not limited to:

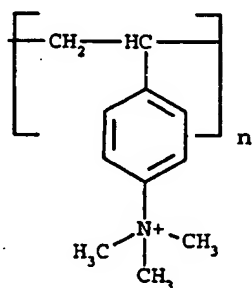
(a) poly(allylamine hydrochloride) (PAH)



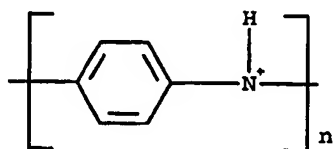
(b) poly(ethyleneimine) (PEI)



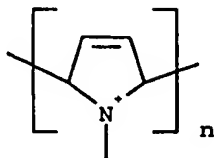
(c) poly(vinylbenzyltrimethylamine) (PVBT)



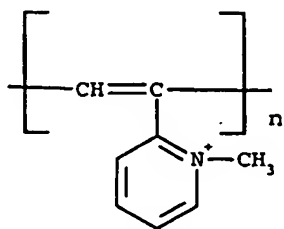
(d) polyaniline (PAN or PANI) (p-type doped) [or sulphonated polyaniline]



(e) polypyrrole (PPY) (p-type doped)

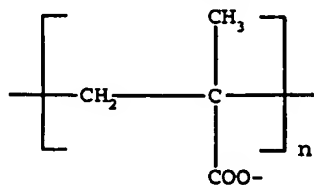


(f) poly(pyridinium acetylene)

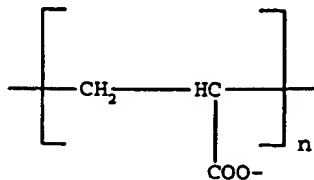


Moreover, a second material may be a polyanionic material, which can generally include any material known in the art to have a plurality of negatively charged groups along a polymer chain. For example, suitable anionic materials can include, but are not limited to:

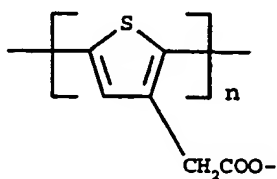
(a) polymethacrylic acid (PMA)



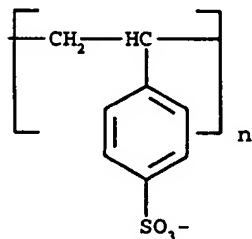
(b) polyacrylic acid (PAA)



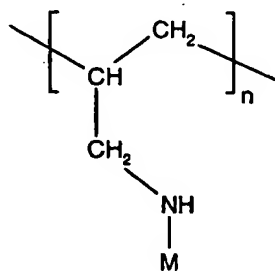
(c) poly(thiophene-3-acetic acid) (PTAA)



(d) poly(4-styrenesulfonic acid) (PSS) or sodium poly(styrene sulfonate) (SPS) or poly(sodium styrene sulfonate) (PSSS)



In certain embodiments, the polycationic material can be made from derivatives of a polyallyl amine having a weight average molecular weight of at least 2000 that, based on the number of amino groups of the polyallyl amine, comprises from approximately 1 to 99% of units having the following formula (1):



(1),

wherein M is a "modifier unit". For instance, in one embodiment, the modifier unit, M, can be R-C=O, where R is C₂-C₆ alkyl that is substituted by two or more same or different substituents selected from the group consisting of hydroxy, C₂-C₅ alkanoyloxy, and C₂-C₅ alkylamino carbonyloxy. Preferably, R is linear C₃-C₆ alkyl, more preferably linear C₄-C₅ alkyl, and most preferably n-pentyl that is in each case substituted as defined above.

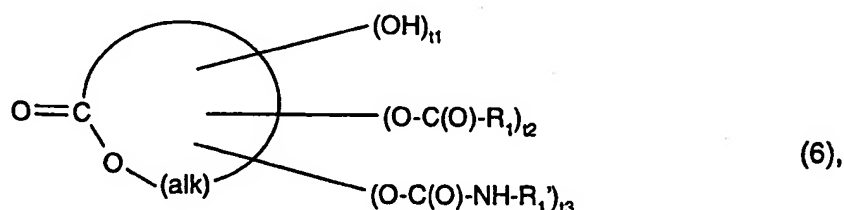
Suitable substituents of the alkyl radical R are -OH, a radical -O-C(O)-R₁, and/or a radical -O-C(O)-NH-R₁', wherein R₁ and R₁' are each independently of the other C₁-C₄ alkyl, preferably methyl, ethyl, iso-, or n-propyl, and more preferably methyl or ethyl. Preferred substituents of the alkyl radical R are hydroxy, acetyloxy, propionyloxy, iso- or n-butanoyloxy, methylaminocarbonyloxy or ethylaminocarbonyloxy, especially hydroxy, acetyloxy, or propionyloxy, and in particular hydroxy.

A particular embodiment of the present invention relates to units of formula (1), wherein R is linear C_p-alkyl comprising "p" same or different above-mentioned substituents, and wherein p is 2, 3, 4, 5, or 6, and preferably 4 or 5, and more preferably 5. Alternatively, R may be C_p-alkyl comprising "p" hydroxy groups that may be partly or completely acetylated, wherein p is 4 or 5, and preferably 6. Particular radicals R are 1,2,3,4,5-pentahydroxy-n-pentyl or 1,2,3,4,5-pentahydroxy-n-pentyl, wherein the hydroxy groups are partly or completely acetylated.

As stated above, embodiments of a polyionic material of the present invention include derivatives of a polyallyl amine that, based on the number of amino groups of the polyallyl amine, comprise from about 1 to about 99%, in some embodiments from about 10 to about 80%, in some embodiments from about 15 to about 75%, and in other embodiments from about 40 to about 60%, of units of formula (1). In general, polyionic materials of the present invention are also water-soluble.

A particular group of polyallyl amine polymers useful in the present invention comprise at least 1%, in some cases at least 5%, and in other cases at least 10% of units of PAH, based on the number of amino groups of the polyallyl amine. Moreover, one group of polyallyl amine polymers may have a weight average molecular weight of, for example, from 2,000 to 1,000,000, from 3,000 to 500,000, from 5,000 to 150,000, or more particularly from 7,500 to 100,000.

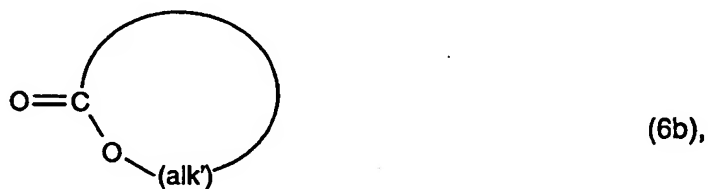
The polyallyl amine polymers described above may be prepared by any manner known in the art. For example, a polyallyl amine having a weight average molecular weight of at least 2,000 that comprises units of PAH may be reacted with a lactone having the following formula (6):



wherein (alk) is linear or branched C₂-C₈-alkylene, the sum of (t₁-t₂-t₃) is at least 1, and R₁ and R₁' as defined above, to yield a polyallyl amine polymer comprising units of formula (1) and PAH.

The reaction between the polyallyl amine and the lactone may be performed in any manner known in the art, such as, by reacting the polyallyl amine with the lactone in an aqueous medium at a temperature from about 20°C to about 100°C, and, in some cases, from 30°C to 60°C. The ratio of units of formula (1) and formula PAH in the final polymer is determined by the stoichiometry of the reactants. The lactones of formula (6) are known or may be prepared according to known methods. Compounds of formula (6), wherein t_2 or $t_3 \geq 1$ are, for example, available by reacting the respective hydroxy compound of formula (6) with a compound $R_1-C(O)X$ or R_1-NCO under conditions well known in the art. Polyallyl amine starting materials of different molecular weights are commercially available, e.g. in the form of the hydrochloride. Hydrochloride can be converted previously into the free amine, for example, by a treatment with a base, such as sodium or potassium hydroxide solution.

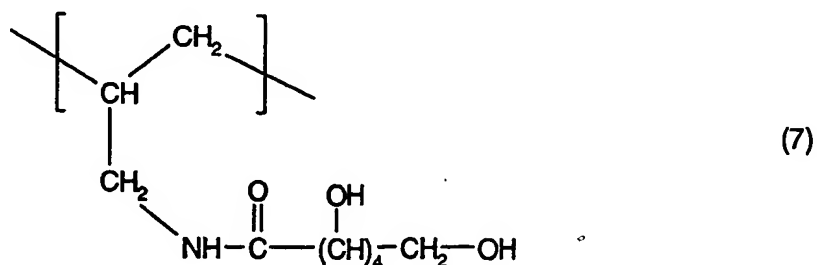
Polyallyl amines comprising additional "modifier units", M, may be prepared by adding to the reaction a mixture of the polyallyl amine and the compound of formula (6), simultaneously or preferably successively. Some examples of compounds that can be added to a polyallyl amine and the compound of formula (6) include, but are not limited to, the following:





wherein X is halogen, preferably chlorine; (alk') is C₁-C₁₂-alkylene; R₁₂ is hydrogen or C₁-C₂-alkyl, preferably hydrogen or methyl; and R₃, R₄, R₅', R₆ and Q₁ are as defined above. The reaction proceeds, for example, in an aqueous solution at room temperature or at an elevated temperature, such as from 25°C to about 60°C, and yields various polymers comprising various modifier units.

Because the reaction of the amino groups of the polyallyl amine with the compounds of formulae (6) or (6a)-(6k) proceeds, in general, quantitatively, the structure of the modified polymers is determined mainly by the stoichiometry of the reactants that are employed into the reaction. A particular polyionic material is polyallylamine gluconolactone, as shown below in formula (7):



The polyallyl amine may be one in which about 20% to about 80% of the amino groups have been reacted with delta-glucolactone to yield R groups of formula (7).

In order to alter various characteristics of the coating, such as thickness, the molecular weight of the polyionic materials can be varied. In particular, as the molecular weight is increased, the coating thickness generally increases. However, if the increase in molecular weight increase is too substantial, the difficulty in handling may also increase. As such, polyionic materials used in a process of the present invention will typically have a molecular weight M_n of about 10,000 to about 150,000. In certain embodiments, the molecular weight is about 25,000 to about 100,000, and in other embodiments from about 75,000 to about 100,000.

In addition to polyionic materials, a coating solution of the present invention can also contain additives. As used herein, an additive can generally include any chemical or material. For example, active agents, such as antimicrobials and/or antibacterials can be added to a coating solution of the present invention, particularly when used in biomedical applications. Some antimicrobial polyionic materials include polyquaternary ammonium compounds, such as those described in U.S. Patent No. 3,931,319 (e.g. POLYQUAD®).

Moreover, others examples of materials that can be added to a coating solution of the present invention are polyionic materials useful for ophthalmic lenses, such as materials having radiation absorbing properties. Such materials can include, for example, visibility tinting agents, iris color modifying dyes, and ultraviolet (UV) light tinting dyes. Still another example of a material that can be added to a coating solution of the present invention is a polyionic material that inhibits or induces cell growth. Cell growth inhibitors can be useful in devices that are exposed to human tissue for an extended time with an ultimate intention to remove (e.g. catheters), while cell growth-inducing polyionic materials can be useful in permanent implant devices (e.g. artificial cornea).

When additives are applied to a coating solution of the present invention, it is generally desired that the additives have some charge. By having a positive or negative charge, the additive can be substituted for one of the polyionic materials in solution at the same molar charge ratio. For example, polyquaternary ammonium compounds typically have a positive

charge. As such, these compounds can be substituted into a solution of the present invention for the polycationic component such that the additive is applied to a substrate material in a manner similar to how a polycationic would be applied.

It should be understood, however, that non-charged additives can also be applied to a substrate material of the present invention. For example, in one embodiment, a polycationic layer can be first applied onto a substrate material. Thereafter, a non-charged additive can be applied and immediately entrapped by a polyanionic material applied thereon. In this embodiment, polyanionic material can sufficiently entrap the non-charged additive between two layers of polyionic material. After such entrapment, the substrate material can then be coated with other layers of polyionic materials in accordance with the present invention. As discussed above, a coating solution of the present invention can generally be formed from polyionic materials and various other chemicals. In one embodiment, a coating solution of the present invention can be a bicomponent solution that contains at least one polycationic and polyionic material. In other embodiments, the coating solution can contain more than two components of a polyionic materials, such as 3, 4, or 5 components.

Regardless of the number of polyionic components present within a coating solution of the present invention, it is typically desired that one of the polyionic components of the solution be present in a greater amount than another component such that a non-stoichiometric solution can be formed. For example, when a polyanionic/polycationic bicomponent solution is formed, either one of the polyionic components can be present in an amount greater than the other component. By forming a solution from polyionic materials in such a manner, a substrate material can be suitably coated with the coating solution in a single dip. Specifically, the non-stoichiometric concentrations of polyionic materials provides a solution that can "self-cascade" such that alternating layers of polyionic materials are formed onto the substrate with a single dip.

To control the amount of each polyionic component within a coating solution, the molar charge ratio can be varied. As used herein, molar charge ratio is defined as the ratio of charged molecules in solution on a molar basis. For example, a 10:1 molar charge ratio can be defined as 10 molecules of a polyanion to 1 molecule of a polycation, or 10 molecules of a polycation to 1 molecule of a polyanion. The molar charge ratio can be determined as defined above for any number of components within a solution, as long as at least one polycation and one polyanion are included therein.

As the molar charge ratio is substantially increased, the structure of the coating on a particular substrate can become more "open". In some instances, such an opening of the coating structure can result in the requirement of more dipping steps to achieve the desired coating on the substrate material. In this regard, a coating solution of the present invention typically has a "molar charge ratio" from about 3:1 to about 100:1. In one embodiment, the coating solution has a molar charge ratio of about 5:1 (polyanion:polycation). In another embodiment, the coating solution has a molar charge ratio of about 1:5 (polyanion:polycation). In still another embodiment, a 3:1 or 1:3 molar charge ratio may be utilized.

In a certain embodiment, the coating solution has a molar charge ratio of about 10:1 (polyanion:polycation). By employing a coating solution having a predominant amount of polyanionic material, a substrate material can be coated in a manner such that the outer layer is a polyanionic material. Substrates having an outer polyanionic material are typically more acidic. It is believed that in some applications, an acidic outer layer can provide a more hydrophilic substrate and allow better wetting. However, it should be understood that an outer layer of polycationic material may also be desirable. In contrast to a polyanionic outer coating, a polycationic outer coating can be achieved by providing a coating solution that contains a predominant amount of polycationic material.

In accordance with the present invention, a coating solution of the present invention is typically maintained at a certain pH level such that the solution remains stable. When the pH of the coating solution is improperly varied, a salt can sometimes form through back-titration. Such precipitation can often have an adverse affect on the ability of the coating solution to coat the substrate layer as desired. As such, depending on the particular coating solution used, the pH of the solution is normally maintained at a value within about ± 0.5 of the appropriate pH range for the solution. In certain embodiments, the pH of the coating solution is maintained at a pH of ± 0.1 of the appropriate pH range for the solution. By maintaining the pH of the solution within a specified range of the appropriate pH for the solution, precipitation can be substantially inhibited.

The appropriate pH range for a coating solution can vary depending on the particular polyionic materials chosen. Any suitable method known in the art can be utilized to

determine the appropriate pH range for a given solution. One such method is described in "Controlling Bilayer Composition and Surface Wettability of Sequentially Adsorbed Multilayers of Weak Polyelectrolytes" by Dougsik Yoo, Seimel S. Shiratori, and Michael R. Rubner, which is published in MACROMOLECULES, Volume 31, Number 13, pages 4309-4318 (1998). For example, in a particular embodiment, a 10:1 (polyanion:polycation) ratio of polyacrylic acid and polyallylamine hydrochloride is utilized. For this particular bicomponent coating solution, the appropriate pH range was determined to be about 2.5.

In accordance with the present invention, a coating solution of the present invention, as described above, can be prepared in a variety of ways. In particular, a coating solution of the present invention can be formed by dissolving the polyionic materials in water or any other material that sufficiently dissolves the material. When a solvent is used, any solvent that can allow the components within the coating solution to remain stable in water is suitable. For example, an alcohol-based solvent can be used. Suitable alcohols can include, but are not limited to, isopropyl alcohol, hexanol, ethanol, etc. It should be understood that other solvents commonly used in the art can also be suitably used in the present invention.

Whether dissolved in water or in a solvent, the concentration of the polyionic materials within a coating solution of the present invention can generally vary depending on the particular materials being utilized, the desired coating thickness, and a number of other factors. However, it may be typical to formulate a relatively dilute aqueous solution of polyionic material. For example, a polyionic material concentration can be between about 0.001% to about 0.25% by weight, between about 0.005% to about 0.10% by weight, or between about 0.01% to about 0.05% by weight.

In this regard, one embodiment a bicomponent coating solution of the present invention can be prepared as follows. However, it should be understood that the following description is for exemplary purposes only and that a coating solution of the present invention can be prepared by other suitable methods.

A bicomponent coating solution can be prepared by first dissolving a single component polyanionic material in water or other solvent at a designated concentration. For example, in one embodiment, a solution of polyacrylic acid having a molecular weight of about 90,000

is prepared by dissolving a suitable amount of the material in water to form a 0.001M PAA solution. Once dissolved, the pH of the polyanionic solution can be properly adjusted by adding a basic or acid material. In the embodiment above, for example, a suitable amount of 1N hydrochloric acid (HCl) can be added to adjust the pH to 2.5.

After preparing the polyanionic solution, the polycationic solution can be similarly formed. For example, in one embodiment, poly(allylamine hydrochloride) having a molecular weight of about 50,000 to about 65,000 can be dissolved in water to form a 0.001M solution. Thereafter, the pH can be similarly adjusted to 2.5 by adding a suitable amount of hydrochloric acid.

The formed solutions can then be mixed to form a single-dip coating solution of the present invention. In one embodiment, for example, the solutions above can be mixed slowly to form the coating solution. The amount of each solution applied to the mix depends on the molar charge ratio desired. For example, if a 10:1 (polyanion:polycation) solution is desired, 1 part (by volume) of the PAH solution can be mixed into 10 parts of the PAA solution. After mixing, the solution can also be filtered if desired.

Once a coating solution is formed in accordance with the present invention, it can then be applied to a substrate material. In one embodiment, a coating solution of the present invention can also be applied to a mold for forming a polymeric material. Thus, although the embodiment discussed below relates to the direct application of a coating solution to the substrate material, other methods of coating the substrate are equally suitable.

Thus, to coat a substrate material, it can be dipped into a coating solution such that the substrate becomes sufficiently coated with the polyionic materials. The coating solution contains both a polyanion and polycation within a single solvent such that a single dip can result in alternating layers of polyionic material. For example, a single dip of a substrate material can result in the substrate being coated with cascaded layers of polyanion/ polycation/ polyanion/ polycation, etc.

In general, a substrate material dipped into a coating solution can be made from any polymeric material, such as contact lenses, molds for forming contact lenses, or shaped polymeric materials. Examples of suitable substrate materials are natural or synthetic

organic polymers, or laminates, composites or blends of said materials, in particular natural or synthetic organic polymers or modified biopolymers which are known in large number. Some examples of polymers are polyaddition and polycondensation polymers (polyurethanes, epoxy resins, polyethers, polyesters, polyamides and polyimides); vinyl polymers (polyacrylates, polymethacrylates, polyacrylamides, polymethacrylamides, polystyrene, polyethylene and halogenated derivatives thereof, polyvinyl acetate and polyacrylonitrile); or elastomers (silicones, polybutadiene and polyisoprene).

A preferred group of materials to be coated are those being conventionally used for the manufacture of biomedical devices, e.g. ophthalmic devices such as intraocular lenses, artificial cornea or in particular contact lenses, which are not hydrophilic per se. Such materials are known to the skilled artisan and may comprise for example polysiloxanes, perfluoroalkyl polyethers, fluorinated poly(meth)acrylates or equivalent fluorinated polymers derived e.g. from other polymerizable carboxylic acids, polyalkyl (meth)acrylates or equivalent alkylester polymers derived from other polymerizable carboxylic acids, or fluorinated polyolefines, such as fluorinated ethylene or propylene, for example tetrafluoroethylene, preferably in combination with specific dioxols, such as perfluoro-2,2-dimethyl-1,3-dioxol. Examples of suitable bulk materials are e.g. Lotrafilcon A, Neoficon, Pasificon, Telefocon, Silafocon, Fluorsilfocon, Paflufocon, Silafocon, Elastofilcon, Fluoroficon or Teflon AF materials, such as Teflon AF 1600 or Teflon AF 2400 which are copolymers of about 63 to 73 mol % of perfluoro-2,2-dimethyl-1,3-dioxol and about 37 to 27 mol % of tetrafluoroethylene, or of about 80 to 90 mol % of perfluoro-2,2-dimethyl-1,3-dioxol and about 20 to 10 mol % of tetrafluoroethylene.

Another group of preferred materials to be coated are amphiphilic segmented copolymers comprising at least one hydrophobic segment and at least one hydrophilic segment which are linked through a bond or a bridge member. Examples are silicone hydrogels, for example those disclosed in PCT applications WO 96/31792 and WO 97/49740 which are herewith incorporated by reference.

A particular preferred group of substrate materials comprises organic polymers selected from polyacrylates, polymethacrylates, polyacrylamides, poly(N,N-dimethylacrylamides), polymethacrylamides, polyvinyl acetates, polysiloxanes, perfluoroalkyl polyethers, fluorinated polyacrylates or -methacrylates and amphiphilic segmented copolymers

comprising at least one hydrophobic segment, for example a polysiloxane or perfluoroalkyl polyether segment or a mixed polysiloxane/perfluoroalkyl polyether segment, and at least one hydrophilic segment, for example a polyoxazoline, poly(2-hydroxyethylmethacrylate), polyacrylamide, poly(N,N-dimethylacrylamide), polyvinylpyrrolidone polyacrylic or polymethacrylic acid segment or a copolymeric mixture of two or more of the underlying monomers. For example, the polymeric materials "A", "B", "C" and "D" described in U.S. Patent No. 5,760,100 are suitable substrate materials for use in the present invention.

In some embodiments of the present invention, the particular substrate material utilized can also be "pre-conditioned" or "oriented" before being dipped into a coating solution.

Although not required, pre-conditioning the substrate material in accordance with the present invention can enhance the "self cascading" of polyionic layers in a single dip process. In particular, pre-conditioning a substrate material typically involves increasing the roughness of the substrate surface.

In this regard, the roughness of the substrate surface can be altered in a variety of ways. Generally, an "underlayer" or "primer layer" of coating solution can be initially applied to the substrate material to accomplish the desired surface alteration. For example, in one embodiment, one or more standard layer-by-layer dip coatings can be employed as an underlayer for the ultimate dip coating of the present invention. The "underlayer" can be applied by any method known in the art, such as by spray-coating, dipping, etc. In some embodiments, the underlayer can be made from a polyionic material, such as poly(ethyleneimine). After applying this primer coating or underlayer, in one embodiment, the substrate can then be dipped into the ultimate coating solution. For instance, in one embodiment, the ultimate coating solution can contain poly(allylamine hydrochloride) and polyacrylic acid. In still another embodiment, the coating solution can contain poly(allylamine hydrochloride) and sodium poly(styrene sulfonate).

Moreover, in another embodiment, the substrate material can be allowed to swell in a solvent solution containing a solvent and at least one polyionic component(s). In general, any solvent that can allow the components within the coating solution to remain stable in water is suitable for use in the present invention. Examples of suitable alcohols can include, but are not limited to, isopropyl alcohol, hexanol, ethanol, etc. In certain embodiments, the substrate material is first allowed to swell in an alcohol solution containing about 20% isopropyl alcohol and about 80% water. In some embodiments, the

alcohol solution used to swell the substrate can also be used as the solvent in the ultimate single-dip polyionic coating solution.

After swelling, the substrate material can then be removed from the solvent solution and allowed to "shrink". This "shrinking" step causes the substrate material to entrap the initial layer of the polycation or polyanion present within the solvent solution. The swelling/-entrapment process described in this embodiment can enhance the ability of the coating solution to coat the substrate material.

It has been discovered that, in most cases, a process of the present invention can apply a coating solution to a substrate material with only a single dip. As such, in contrast to the aforementioned LbL process, a process of the present invention can apply a coating in relatively little time. For example, coatings can be applied in a time period as little as one minute. Moreover, in some applications, a 100 angstrom coating can be applied in about 6 minutes using a single dip, whereas a similar coating could take approximately 10 hours to apply using the aforementioned LbL process (e.g. 20 dips). Moreover, it has been discovered that, in certain applications, a process of the present invention can apply coatings from about 40 angstroms to about 2000 angstroms in a single dip.

However, it may often be desired to apply a coating having a substantial thickness that cannot be sufficiently applied with a single dip. For example, in one embodiment of the present invention, a 500 angstrom coating is applied to a substrate material in two dipping steps. In particular, a 10:1 polyanion to polycation dip is first applied to the substrate material. Thereafter, a 1:10 polyanion to polycation is employed as a second coating layer. In some embodiments, more than two dips, such as 3 to 5 dips in multi-component solutions of the present invention can be utilized. For example, when coating a contact lens material according to the present invention, three dips may be utilized. However, even when more than one dipping step is utilized with solutions of the present invention, the substrate material can still be coated in substantially less time than with a LbL process. In fact, a LbL process could take approximately 50 hours (e.g. 100 dips) to apply a 500 angstrom coating, while a process of the present inventive single dip process can take approximately 8 to 30 minutes (e.g. 4 or 5 dips) to achieve the same thickness.

In one embodiment of the present invention, the single-dip solution can also be utilized for coating of a mold used to define the shape of an article. Coating a mold in this manner can prove useful in processes such as transfer grafting a polyionic coating. In one embodiment, the mold is coated with a polyionic solution of the present invention, but at least a portion of the coating is transferred from the mold when the liquid molding material (e.g., polymerizable material) is dispensed into the mold for formation of the solid article. Hence, another embodiment of the invention is a method of forming an article and coating the article by transfer grafting a coating material from the mold in which the article was produced. This method includes the steps of applying a coating of a polyionic solution to a mold by contacting at least a portion of the mold with the solution, dispensing a liquid molding material into the mold, thereby contacting said liquid molding material with said coating, allowing the mold coating to contact the liquid molding material during curing and causing the liquid mold material to harden (e.g., by polymerization via application of UV light). As a result, the coating can remain in tact and transfer to the solidified article.

The present invention may be better understood by reference to the following examples.

EXAMPLE 1

The ability of polyionic materials to be coated onto a contact lens in a relatively short amount of time using a solution of the present invention is demonstrated. The substrate material (i.e. contact lens) is prepared with materials, such as described in U.S. Patent No. 5,760,100.

A sample contact lens (polysiloxane/perfluoroalkylpolyether copolymer) is coated using single dip solutions of the present invention. In particular, the lens is coated as follows. Initially, a primer layer is applied to the lens by spraying a PEI solution onto the lens for 1 minute (using an ultrasonic nozzle), drying the lens for 1 minute (using an air knife), spraying with a PAA solution for 1 minute, drying for 1 minute, spraying with a PEI solution for 1 minute, drying for 1 minute, spraying with a PAA solution for 1 minute, and drying for 1 minute. The PEI and PAA solutions are prepared by dissolving the respective powders in water to form 0.001M solutions.

After applying the primer coating, the lens is dipped in a predominantly polyanionic single-dip solution for 1 minute, dried for 1 minute, dipped into a predominantly polycationic single-dip solution for 1 minute, and dried for 1 minute such that a 10 bilayer coating is formed. The single-dip solutions used above are formed as follows. A solution of polyacrylic acid

having a molecular weight of about 90,000 is prepared by dissolving a suitable amount of the material in water to form a 0.001M PAA solution. Once dissolved, the pH of the polyanionic solution is adjusted by adding 1N hydrochloric acid until the pH reaches 2.5. After preparing the above solution, poly(allylamine hydrochloride) having a molecular weight of about 50,000 to about 65,000 is dissolved in water to form a 0.001M solution. Thereafter, the pH is similarly adjusted by adding hydrochloric acid until a pH of 2.5 is obtained.

A portion of the solutions are then mixed to form the predominantly polyanionic single-dip coating solution. Specifically, a single-dip solution having a 10:1 molar charge ratio (polyanion:polycation) is formed by adding 1 part (by volume) of the PAH solution into 10 parts (by volume) of the PAA solution. The predominantly polycationic single-dip solution is similarly formed into a solution having a 1:10 molar charge ratio (polyanion:polycation) by adding 1 part (by volume) of the PAA solution into 10 parts (by volume) of the PAH solution. It is determined that only 4 spray steps (primer layer) and 2 dips, taking only 12 minutes, are needed to form about a 1 micron coating on the lens. As can be seen from the results of the example, a single-dip solution of the present invention can allow the coating of substrate materials in faster times than standard layer by layer processes.

EXAMPLE 2

The ability of polyionic materials to be first coated onto a mold so that a contact lens can be formed within the mold and the coating can transfer from the mold to the contact lens is demonstrated. The substrate material (i.e. contact lens) is prepared with materials, such as described in U.S. Patent No. 5,760,100 to Nicolson et al. and the molds are made by cast molding techniques, such as described herein.

A sample mold is initially coated with a primer layer by spraying a PAA solution onto the lens for 1.5 seconds using an ultrasonic nozzle. The PAA solution is prepared as described in Example 1. After spraying, the mold is sprayed with water for 3 seconds. Thereafter, the mold is sprayed with a PEI solution for 1.5 seconds followed with water for 3 seconds. The PEI solution is prepared as described in Example 1. The mold is again sprayed with the PAA solution for 1.5 seconds and water for 3 seconds. A PAH solution is then sprayed onto the mold for 1.5 seconds, followed by a water spray for 3 seconds. The PAH solution is prepared by dissolving PAH powder in water to form a 0.001M solution. Once the above steps are completed, the mold is again sprayed with a PAA solution for 1 minute, sprayed with water for 3 seconds, sprayed with a PAH solution for 1.5 seconds, sprayed with water

for 3 seconds, sprayed with a PAA solution for 1.5 seconds, sprayed with water for 3 seconds, sprayed with a PAH solution for 1.5 seconds, sprayed with water for 3 seconds, sprayed with a PAA solution for 1.5 seconds, sprayed with water for 3 seconds, sprayed with PAH for 1.5 seconds, sprayed with water for 3 seconds, etc., until 5 bilayers of polyionic material are formed onto the mold.

Once the molds are coated, a polymeric substrate material, such as disclosed herein, is then dispensed into the mold. Thereafter, the polymeric substrate material is cast, cured, and extracted through isopropyl alcohol extraction as is well known in the art. After being removed, the sample lens is dipped into a predominantly polyanionic single-dip solution for 2 to 5 minutes.

The single-dip solution used above is formed as follows. A solution of polyacrylic acid having a molecular weight of about 90,000 is prepared by dissolving a suitable amount of the material in water to form a 0.001M PAA solution. Once dissolved, the pH of the polyanionic solution is adjusted by adding 1N hydrochloric acid until the pH reached 2.5. After preparing the above solution, poly(allylamine hydrochloride) having a molecular weight of about 50,000 to about 65,000 is dissolved in water to form a 0.001M solution. Thereafter, the pH is similarly adjusted by adding hydrochloric acid until a pH of 2.5 is obtained. A portion of the solutions is then mixed to form the predominantly polyanionic single-dip coating solution. Specifically, a single-dip solution having a 10:1 molar charge ratio (polyanion:polycation) is formed by adding 1 part (by volume) of the PAH solution into 10 parts (by volume) of the PAA solution.

It is determined that a 5 bilayer coating is achieved with a spray time of 1.5 minutes and a dip time of 2 to 5 minutes to form a 200 to 400 angstrom coating. Moreover, it is also determined that essentially the entire coating transferred to the solidified article.

EXAMPLE 3

The ability of polyionic materials to be transferred from a mold to a contact lens formed within the mold is demonstrated. The substrate material (i.e. contact lens) is prepared with materials, such as described in U.S. Patent No. 5,760,100 and the molds are made by cast molding techniques, such as described herein.

A sample mold is initially coated with a primer layer by spraying a PAA solution onto the lens for 1.5 seconds using an ultrasonic nozzle. The PAA solution is prepared as described in Example 1. After spraying, the mold is sprayed with water for 3 seconds. Thereafter, the mold is sprayed with a PEI solution for 1.5 seconds followed with water for 3 seconds. The

PEI solution is prepared as described in Example 1. The mold is again sprayed with the PAA solution for 1.5 seconds and water for 3 seconds. A PAH solution is then sprayed onto the mold for 1.5 seconds, followed by a water spray for 3 seconds. The PAH solution is prepared by dissolving PAH powder in water to form a 0.001M solution.

Once the above steps are completed, the mold is dipped into a predominantly polyanionic single-dip solution for 5 minutes, rinsed with water for 1 minute, dipped into a predominantly polycationic single dip solution for 1 minute, and rinsed with water for 1 minute. After applying the coating to the mold, a polymeric substrate material is dispensed into the mold, cured, and extracted as described in Example 2. Thereafter, the finished contact lens is dipped into a predominantly polyanionic single dip solution for 2 to 5 minutes.

The single-dip solutions used above are formed as described in Example 1.

It is determined that a 5 bilayer coating having a thickness of approximately 1 micron can be formed in 13 minutes for each lens.

EXAMPLE 4

A contact lens (polysiloxane/perfluoroalkylpolyether copolymer) is coated by just one dip using an embodiment of the single dip solution described herein. In particular, the lens is coated after it was allowed to swell in isopropyl alcohol (IPA). After 2 to 5 minute soak, the lenses are removed from the alcohol solution and then dipped for approximately 5 min into a 0.001M solution containing both polyacrylic acid having a molecular weight of about 90,000 and poly(allylamine hydrochloride) having a molecular weight of about 60,000 at a 10:1 molar charge ratio (polyanion/polycation) and a pH of 2.5. After dipping, the lenses are placed in phosphate buffered saline and autoclaved (sterilized).

The single-dip solution employed in this Example is prepared as follows: A solution of polyacrylic acid having a molecular weight of about 90,000 is prepared by dissolving a suitable amount of the material in water to form a 0.001M PAA solution. Once dissolved, the pH of the polyanionic PAA solution is adjusted by adding 1N hydrochloric acid until the pH reaches 2.5. Then, a solution of poly(allylamine hydrochloride) having a molecular weight of about 60,000 is prepared by dissolving a suitable amount of the material in water to form a 0.001M PAH solution. Thereafter, the pH of the polycationic PAH solution is similarly adjusted by adding 1N hydrochloric acid until a pH of 2.5 is obtained.

A portion of the PAA and PAH solutions are then mixed to form the predominantly polyanionic single-dip coating solution. Specifically, a solution having a 10:1 molar charge

ratio (polyanion/polycation) is formed by adding 1 part (by volume) of the PAH solution into 10 parts (by volume) of the PAA solution.

It is determined that a hydrophilic coating on a contact lens with a contact angle of 50 or less can be achieved by just one 5 minute or less dip in a single-dip solution of the present invention.

EXAMPLE 5

The ability of polyionic materials to be deposited onto a contact lens mold is demonstrated. Various contact lenses are coated using different coating methods. For each lot below, the substrate material (i.e. contact lens) is prepared with materials, such as described in U.S. Patent No. 5,760,100 and the molds are made by cast molding techniques, such as described herein.

Dip coated lenses (Lot #1): The first lot of contact lenses is prepared by dipping the lenses into the polyionic materials. Initially, the contact lenses are swelled in an isopropyl alcohol solution. After sufficient swelling, the lenses are then dipped into a .001M solution (Solution A) that contains poly(allylamine hydrochloride) having a MW of about 60,000 and polyacrylic acid having a MW of about 90,000 at a 10:1 molar charge ratio (polyanion/polycation) and a pH of 2.5. The lenses remain in the solution for 5 minutes and are thereafter rinsed with water for approximately 1 minute. After dipping the lenses into Solution A and rinsing, the lenses are dipped into a second .001M solution (Solution B) that contains the same polyionic materials and pH, but having a molar charge ratio of 1:10 (polyanion/polycation). The lenses remain in this solution for 5 minutes. After dipping, the lenses are rinsed for about 1 minute with water.

Spray coated molds (Lot #2): The second lot of contact lenses is prepared by spraying molds with polyionic materials prior to forming the lenses. The molds are sprayed with a 0.001M solution that contains poly(ethyleneimine) for about 1 minute using an ultrasonic nozzle. Thereafter, the lenses are rinsed and sprayed with a .001M solution of polyacrylic acid for about 1 minute. These steps are repeated into 3 bilayers are formed onto the mold. After applying the sprayed coating, the lens materials are dispensed into the molds and cured. The lenses are then extracted with isopropyl alcohol.

Dip coated molds (Lot #3): The third lot of contact lenses is prepared by dipping the sprayed molds above into other solutions of polyionic materials. After being sprayed, the molds are dipped into Solution A for about 5 minutes, rinsed in water for about 1 minute, dipped into Solution B for about 5 minutes, and rinsed again in water for about 1 minute.

After dipping, the lens materials are dispensed into the molds and cured. The lenses are then extracted with isopropyl alcohol, dipped into Solution A for about 5 minutes, and then dipped into Solution B for about 5 minutes.

Surface properties of the lenses are then evaluated.

(i) The IP values measure the ion permeability of a particular contact lens when contacted with salt ions and water. In other words, the IP value measures the ability of ions to diffuse through the contact lens. This test is more specifically described in U.S. Patent No.

5,760,100.

(ii) The Dk value is generally a measure of the ability of a gas, such as oxygen, to diffuse through a contact lens. A more detailed description of the Dk value can also be obtained by reference to U.S. Patent No. 5,760,100.

(iii) The average contact angles (Sessle Drop) are measured using a VCA 2500 XE contact angle measurement device from AST, Inc., located in Boston, Massachusetts. The contact angles generally measure the surface energy of a contact lens.

(iv) The NISDT, or non-invasive surface drying time, is determined. The NISDT is a measure of the break up time of a particular contact lens. In particular, each contact lens is visually observed while being worn via a slit lamp, a commonly used measuring device. The NISDT is determined at the point the first disruption of the tear film was observed.

(v) Subjective results are determined from test subjects as to the comfort of each lens.

The lenses of the three lots all show values concerning IP, Dk, Contact angle, NISDT and Comfort which make them suitable for extended wear on the eye.

Although various embodiments of the invention have been described using specific terms, devices, and methods, such description is for illustrative purposes only. The words used are words of description rather than of limitation. It is to be understood that changes and variations may be made by those of ordinary skill in the art without departing from the spirit or scope of the present invention, which is set forth in the following claims. In addition, it should be understood that aspects of the various embodiments may be interchanged both in whole or in part. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained therein.

WHAT IS CLAIMED IS:

1. A method of coating a polymeric substrate comprising the steps of:
forming a solution, said solution containing a negatively charged material and a positively charged material in an amount such that the molar charge ratio of said solution is from about 3:1 to about 100:1;
maintaining the pH of said solution within a range so that said negatively charged material and said positively charged material remain stable within said solution; and
applying said solution to said substrate to form a coating thereon, said coating on said substrate having at least two layers so that one of said layers comprises said negatively charged material and another of said layers comprises said positively charged material.
2. A method as defined in claim 1, wherein said molar charge ratio is about 10:1.
3. A method as defined in claim 1 or 2, wherein the negatively charged material comprises a polyacrylic acid.
4. A method as defined in any of claims 1 to 3, wherein the negatively charged material comprises an additive selected from the group consisting of an antimicrobial and an antibacterial.
5. A method as defined in any one of claims 1 to 4, wherein the positively charged material comprises a poly(ethyleneimine) or poly(allylamine hydrochloride).
6. A method as defined in any one of claims 1 to 5, wherein the negatively charged material comprises polyacrylic acid and the positively charged material comprises a poly(allylamine hydrochloride), and wherein the pH of said solution containing said polyacrylic acid and said poly(allylamine hydrochloride) is maintained at a value of about 2.5.
7. A method as defined in any one of claims 1 to 6, wherein said positively charged material comprises an additive selected from the group consisting of an antibacterial and an antimicrobial.

8. A method as defined in any one of claims 1 to 7, wherein the negatively charged material predominates said solution.
9. A method as defined in any one of claims 1 to 7, wherein the positively charged material predominates said solution.
10. A method as defined in any one of claims 1 to 9, wherein the pH of said solution is maintained within ± 0.5 , preferably within ± 0.1 , of an appropriate pH range, said appropriate pH range being dependent on the selection of said negatively charged material and said positively charged material.
11. A method as defined in any one of claims 1 to 10, further comprising the step of preconditioning said substrate before dipping said substrate into said solution, wherein said substrate is preconditioned with a primer coating, said primer coating being applied to said substrate by dipping said substrate into a solution containing primer materials.
12. A method as defined in claim 11, wherein said substrate is preconditioned by the steps of:
providing a solvent solution comprising a solvent and at least one polyionic material;
allowing said substrate to swell in said solvent solution;
removing said substrate from said solvent solution after said substrate swells therein; and
allowing said substrate to shrink such that said at least one polyionic material becomes entrapped within said substrate.
13. A method as defined in claim 12, wherein said solvent comprises an alcohol, preferably isopropyl alcohol.
14. A method as defined in any one of claims 1 to claim 13, wherein the thickness of said coating is from about 40 angstroms to about 2000 angstroms.
15. A method as defined in any one of claims 1 to 14, wherein said substrate is dipped into said solution such that a coating forms thereon.

16. A method as defined in claim 15, wherein said substrate is coated with said solution in one dip.

17. A method as defined in claim 15, where said substrate is coated with said solution in 2 to 5 dips.

18. A method as defined in any one of claims 1 to 17, wherein said substrate comprises a mold and further comprising the steps of:

dispensing a polymeric material into said mold;

curing said polymeric material so that said coating detaches from said mold during curing and at least partially attaches to the exterior surface of said polymeric material; and

removing said cured polymeric material from said mold, said polymeric material being coated with at least a portion of said solution.

19. A method of coating a polymeric material comprising the steps of:

forming a polyionic solution, said polyionic solution containing a polyanionic material and a polycationic material in an amount such that the molar charge ratio of said solution is less than about 10:1;

maintaining the pH of said solution within a range so that said polyanionic and polycationic materials remain stable within said polyionic solution;

providing a substrate;

applying a solvent to said substrate, said solvent being capable of forming a stable solution when combined with said solution containing said polyanionic and said polycationic materials;

allowing said substrate to swell in said solvent;

removing said substrate from said solvent after swelling said substrate therein; and

dipping said substrate into said solution to form a coating thereon, said coated substrate having at least two layers with one of said layers comprising said polyanionic material and another of said layers comprising said polycationic material.

20. A method of coating a contact lens comprising the steps of:

forming a polyionic solution, said solution containing a polyanionic material and a polycationic material in an amount such that the molar charge ratio of said solution is less than about 10:1;

maintaining the pH of said solution within a range so that said polyanionic and polycationic materials remain stable within said solution; and
dipping said contact lens into said solution to form a hydrophilic coating thereon, said coated substrate having at least two layers such that one of said layers comprises said polyanionic material and another of said layers comprises said polycationic material.

21. A method of coating a polymeric material comprising the steps of:

providing a substrate;

applying a first polyionic material to said substrate, said first polyionic material having a certain charge;

applying an additive to said substrate, said additive having substantially no charge;

applying a second polyionic material to said substrate after applying said additive thereto, said second polyionic material having a charge opposite to said charge of said first polyionic material;

applying a solution to said substrate to form a coating thereon, said solution containing a polyanionic material and a polycationic material in an amount such that the molar charge ratio of said solution is from about 3:1 to about 100:1, wherein the pH of said solution is maintained within a range so that said polyanionic material and said polycationic material remain stable within said solution; and

said coated substrate having at least two layers such that one of said layers comprises said polyanionic material and another of said layers comprises said polycationic material, said two layers substantially entrapping said additive on said coated substrate.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR COATING A SURFACE

(57) Abstract: A method of forming a coating of polyionic materials in a layer-by-layer-like manner onto a polymeric material is provided. A polymeric material, such as a contact lens, can be dipped once into a solution of polyionic materials such that layers of polyionic material can be formed thereon. A single dip solution of the present invention typically contains a polyanionic material and a polycationic material in a non-stoichiometric amount and maintained within a certain pH range.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/01154

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08J7/04 A61L27/34 A61L27/40 A61L27/44 G02B1/04
B05D1/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J A61L G02B B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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E	WO 01 27209 A (DAVIES MARTYN CHRISTOPHER ;CLARKE STUART (GB); BIOCOMPATIBLES LTD) 19 April 2001 (2001-04-19) claims 1-20 ----	1
A	WO 99 35520 A (NOVARTIS ERFINDE VERWALT GMBH ;NOVARTIS AG (CH); VOGT JUERGEN (CH);) 15 July 1999 (1999-07-15) claims 1-38 ----	1
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

S document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

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